

Synthesis and Performance Study of Self-Degradable Gel Plugging Agents Suitable for Medium- and Low-Temperature Reservoirs

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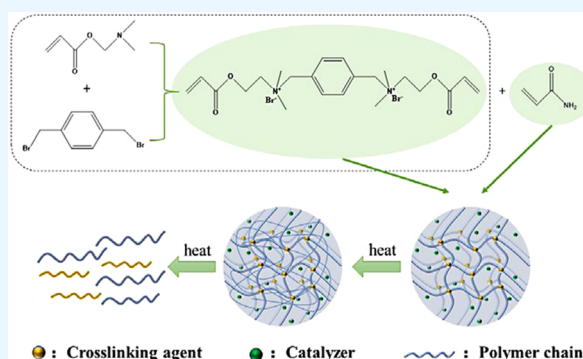
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ABSTRACT: Aiming at the problems of current similar hydrogel plugging agents, such as poor breaking performance, nonspontaneous degradation, and reservoir pollution which have been plaguing their application in temporary plugging operations, this study has synthesized a cross-linking agent for hydrogels with dimethylaminoethyl acrylate and dibromo-*p*-xylene as raw materials. With Fourier transform infrared, ¹H nuclear magnetic resonance, and thermogravimetric analyses as representations of the structure and thermal stability of the cross-linking agent, a set of self-degrading hydrogel systems has been developed with the cross-linking agent as the core so as to make evaluations on the temperature resistance, plugging performance, and core damage performance of the hydrogel and conduct a study on its gelation kinetics. The research results show that the cross-linking agent shows good thermal stability. When applied in the hydrogel system, the hydrogel has shown high temperature resistance, maintaining gel strength for 5–10 days at 50–90 °C, with viscosity after complete degradation lower than 10 mPa·s. The excellent bearing strength of the hydrogel system has led to a core damage rate below 5%. The study on gelation kinetics of the hydrogel system shows that, with the increase in the concentration of the cross-linking agent, the gelation time of the hydrogel system is shortened, with the reaction order between the cross-linker concentration and the gelation time at about 0.6 under the condition of 50–90 °C.



1. INTRODUCTION

At present, the water injection development mode has been generally adopted by oilfields both at home and abroad. With the deepening of development, a large number of pressurized water injection wells need string inspection and workover operations every year, and the operation demand is huge.^{1–3} The traditional well-killing method uses well control fluid, which suffers from many defects including the possible pollution of the formation by the fluid, the lowering of the permeability of the reservoir, etc., and the well-killing fluid operation is exposed to great risks.^{1,4,5}

Since the Tuha Engineering Institute proposed the gel plugging technology under pressure in 2007, many scholars have carried out research on this technology, and the feasibility of this technology has been verified through field experiments.^{6–9} With the rise of polymer chemistry, polymer gel technology has achieved long-term development, giving birth to hydrogel materials with good pregelling rheological properties, characterized by easy injection, postgelling deformability, and adjustable plugging strength.^{10–12} Therefore, polymer gels boast unique advantages in plugging operations.^{13–15} Due to its high deformability, it is not restricted by the leakage channel. After injection, it can be

cross-linked and copolymerized from an easy-flowing polymer or monomer solution to form immobile jelly or gel, which can produce a plugging effect in extremely small pores. This material, in a liquid state before injection, is transformed into a solid gel with a three-dimensional network structure due to the cross-linking effect under the formation conditions after injection, which means an excellent plugging effect.^{16–19}

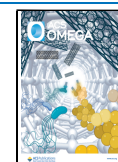
At present, the commonly used polymer gel systems are mainly cross-linked polymer gels based on polyacrylamide and modified cross-linked polymer gels based on acrylamide.^{20,21} Freedman et al. have developed a series of degradable hydrogels by combining covalent network degradable cross-linking agents and hydrolyzable ionic cross-linked backbone polymers, and these hydrogels have shown high mechanical properties, adhesion, and degradability in tests up to 16 weeks;²² Jia et al. have studied a new type of high-strength

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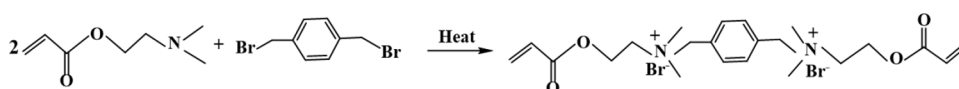


Figure 1. Schematic diagram of the synthetic route of the cross-linking agent.

degradable nanocomposite gel, and this system can be gelled within 20–50 min at 75 ~ 105 °C, boasting excellent shear resistance.²⁴ However, the existing similar hydrogel plugging agents cannot be easily adopted in medium and low-temperature plugging operations due to problems such as poor breaking performance, nonspontaneous degradation, and reservoir pollution, leading to great difficulty and high risks in on-site constructions.^{23–27} Quaternary ammonium ester cross-linkers are an important class of cross-linkers for hydrogels, and compared to other common cross-linkers, quaternary ammonium ester cross-linkers applied to hydrogels can achieve low- and medium-temperature self-degradation.^{28–33}

To solve this problem, this article synthesized a new quaternary ammonium ester cross-linking agent from dibromo-*p*-xylene, a monomer containing a temperature-resistant group benzene ring, which is represented through FT-IR, ¹H NMR, and TGA; a high-strength self-degrading hydrogel has been prepared with acrylamide and a cross-linking agent, and the basic formula of the hydrogel has been optimized through single-factor experiments. The temperature resistance, plugging capacity, and reservoir protection performance of the hydrogel have been examined with the gelation kinetics of the hydrogel system under different cross-linking agent concentrations and polymerization temperatures studied.

2. EXPERIMENT MATERIALS AND METHODS

2.1. Materials. Acrylamide (AM, 99.0%), dimethylaminoethyl acrylate (DMAEA, 99.5%), phenothiazine (>99%), and dibromo-*p*-xylene (>99%) were purchased from Shanghai Maclin Biochemical Technology Co., Ltd; ammonium persulfate (APS, ≥98.0%), ether (>99%), and methanol (>99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China); all the chemicals are analytical reagents to be used with no further purification.

2.2. Preparation of Hydrogels. **2.2.1. Synthesis of the Cross-Linking Agent.** A white paste was obtained by dissolving 10 g of dimethylamino ethyl acrylate in an equal mass of methanol solution, followed by the addition of 6.48 g of dibromo-*p*-xylene and 0.1% (of the total mass) of phenothiazine, respectively, after stirring evenly. Subsequently, it was placed in a 45 °C water bath and stirred for 48 h to obtain a white paste. After cooling, it was washed with ether 3 times, recrystallized in ethanol, filtered with suction, and dried to obtain the cross-linking agent. The synthetic route is depicted in Figure 1 below.

2.2.2. Preparation of Hydrogels. The synthesis of the hydrogel is determined by reference to Zou et al. and is improved upon on its basis.³² The specific experimental steps are as follows: the hydrogel base solution is prepared at room temperature by first dissolving the acrylamide and the synthesized cross-linking agent in distilled water. The mixture is stirred for 30 min at a stirring speed of 400 rpm, and then, the initiator ammonium persulfate is added after homogenization, followed by continued stirring for 10 min. Subsequently, the hydrogel base solution is transferred into an ampule, and the sealed ampule is placed in a constant-temperature water bath for heating. This results in the gel

being a temporary plugging agent obtained when the solution is completely solidified.

2.3. Performance Evaluation of Hydrogels. **2.3.1. Representations of Cross-Linking Agents.** The WQF-520 Fourier transform infrared spectrometer is used for measurement, KBr pellets for pressing, and the chemical structure changes of the cross-linking agent are represented via FT-IR analysis.

A Bruker 400 M nuclear magnetic resonance spectrometer is used for measurement, with D₂O as the solvent, the mass concentration of the cross-linking agent is about 1 g/L, with its chemical structure analyzed via ¹H NMR.

A STA449F5 synchronous thermal analyzer is used for measurement, and the thermal stability of the cross-linking agent is evaluated by raising the temperature from room temperature to 600 °C at a rate of 10 °C/min under a nitrogen atmosphere.

2.3.2. Representation of Hydrogels. The WQF-520 Fourier transform infrared spectrometer is used for measurement and KBr for pressing, with the chemical structure changes of the hydrogels represented via FT-IR analysis.

The STA449F5 synchronous thermal analyzer is adopted for measurement, and the thermal stability of the hydrogel temporary plugging agent is evaluated by raising the temperature from room temperature to 600 °C at a rate of 10 °C/min under a nitrogen atmosphere.

2.3.3. Performance Evaluation of Hydrogels. **2.3.3.1. Determination of the Gelation Time and Degradation Time of Hydrogels.** The prepared hydrogel base solution was injected into an ampule under atmospheric pressure and temperature, and the sealed ampule was placed in a constant temperature water bath at 50–90 °C to fully react, and the hydrogel gelation time and degradation time were measured by the gel strength code (GSC) method, which was used to measure the hydrogel formation time and degradation time.¹⁹ In this study, the time for the hydrogel to reach grade E is defined as the gelation time, while the time for the hydrogel to reach grade C is defined as the degradation time.

2.3.3.2. Evaluation of Temperature Resistance. The prepared hydrogel systems were put in constant-temperature water baths at 50, 60, 70, 80, and 90 °C, respectively, to examine the gelation performance and degradation time of the hydrogels under different temperatures. Upon complete degradation of the hydrogel, the viscosity of the degradation solution is tested with a Brookfield DV-3T viscometer under corresponding temperature conditions. A CPA-41Z rotor has been selected for the test process, and the shear rate ranges from 1 to 100 s⁻¹.

2.3.3.3. Plugging Performance Evaluation. The displacement device is used to evaluate the plugging performance of the hydrogel. The specific experimental steps are as follows: the prepared hydrogel base solution is injected into the sand filling tube at the rate of 1 mL/min, the sand filling tubes are put into the constant temperature oven at the required temperature to form glue, and then, they are taken out (50–90 °C). It is tested that the injected hydrogel base solution is 0.25, 0.5, 0.75, and 1 PV of the total injected amount. The nitrogen cylinder is connected to the outlet end of the sand-filled pipe,

and reverse injection is used to test the bearing performance of the hydrogel and conduct real-time monitoring of the pressure changes.

2.3.3.4. Formation Protection Performance. Core injuriousness is an important index for evaluating the protection performance of the hydrogel to the formation after degradation; in this study, we adopt the core expulsion experiment to evaluate the formation protection performance of hydrogel, and the length of the fractured core used is 10 cm, and the diameter is 2.5 mm, and the specific experimental steps are as follows: (1) the experimental apparatus is connected and its sealing with deionized water is tested; (2) the initial permeability K_1 of the fractured core was measured by placing the fractured core into the core gripper, loading the annulus with a pressure of 3.0 MPa and injecting simulated formation water at 1 mL/min; (3) the hydrogel base solution was injected at a rate of 1 mL/min (the volume of the injected hydrogel base solution was equal to the fracture volume of the fractured core used), and the perimeter pressure needed to be kept always higher than the injection pressure of 3.0 MPa during the experiment; (4) the pump was stopped, the valve was turned off, and the core gripper was placed under the desired temperature conditions (50–90 °C), during which the hydrogel base solution will go through the three phases of gel formation, blocking and degradation; (5) after the hydrogel in the core holder is completely degraded, the permeability K_2 of the fractured core is measured; and (6) the core damage rate is calculated, and the formula for the core damage rate is shown in the following equation.

$$\sigma = \left(\frac{K_1 - K_2}{K_1} \right) \times 100\%$$

In the formula, σ represents the plugging rate, K_1 represents the initial permeability of the fractured core, μm^2 , and K_2 represents the permeability of the fractured rock after the complete degradation of the hydrogel, μm^2 .

2.3.3.5. Hydrogel Gelation Kinetic Analysis. The relationship between the gelation time of the hydrogel and the cross-linker concentration is recorded. With GT as the gelation time of the gel system and P as the mass concentration of the cross-linking agent, $\log(\text{GT})$ and $\log(P)$ are plotted to form straight lines for fitting, and the slope obtained is the order of reaction corresponding to the polymer in the gelation process of the system.

3. RESULTS AND DISCUSSION

3.1. Representations of Cross-Linking Agents.

3.1.1. FT-IR Analysis. The infrared spectra of dibromo-*p*-xylene, DMAEA, and the cross-linking agent are shown in Figure 2. As can be seen from Figure 2, the =C–H vibrational absorption peak of the benzene ring is at 3008 cm^{-1} in the infrared diagram of dibromo-*p*-xylene. The stretching vibration peak of C–H in the double bond is at 2985 cm^{-1} in the DMAEA infrared spectrum, the stretching vibration peak of C=O in the ester bond is at 1727 cm^{-1} , the deformation vibration peak of N–H in the amine group is at 1638 cm^{-1} , and the symmetric vibration absorption peak of C–O is at 1193 cm^{-1} . In the infrared spectrum of the cross-linking agent, the stretching vibration absorption peaks of N–H are at 3523 and 3410 cm^{-1} , the stretching vibration peak of C–H in the double bond is at 3270 cm^{-1} , the stretching vibration absorption peak of C–H in the benzene ring is at 3010

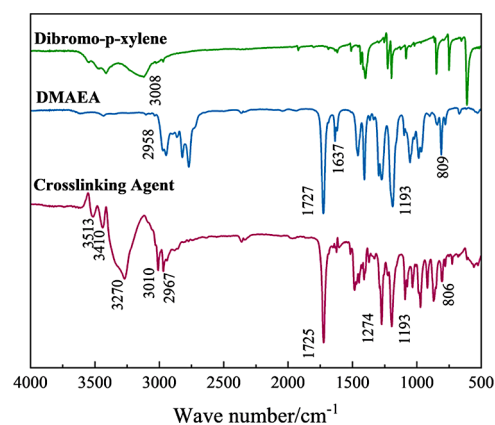


Figure 2. Infrared spectra of dibromo-*p*-xylene, DMAEA, and cross-linking agent.

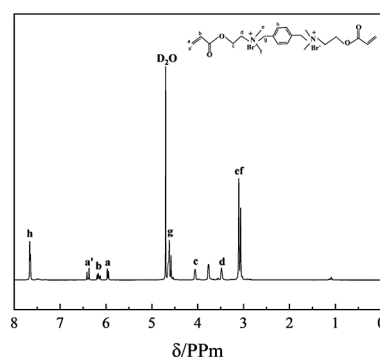


Figure 3. ^1H NMR spectrum of the cross-linking agent.

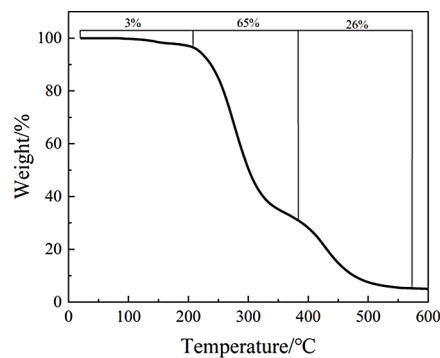


Figure 4. Thermogravimetric curve of the cross-linking agent.

cm^{-1} , the characteristic absorption peak of quaternary amine groups is at 2967 cm^{-1} , and the stretching vibration peak of C=O in the ester bond is at 1725 cm^{-1} ; the vibration absorption peak at 1623 cm^{-1} is C=C. At 1274 and 1193 cm^{-1} , there are antisymmetric and symmetric vibration absorption peaks for C–O, respectively. At 809 cm^{-1} , there is an out-of-plane bending vibration peak for the C–H in the double bond. Through the infrared spectrum, it can be observed that characteristic absorption peaks of the benzene ring, carbon–carbon double bond, ester group, and quaternary amine group appear in the infrared spectrum of the cross-linking agent, indicating the successful synthesis of the target cross-linking agent.

3.1.2. ^1H NMR Analysis. The ^1H NMR spectrum of the cross-linking agent is shown in Figure 3 which indicates the chemical shift of the carbon–carbon double bond at 6.41, 6.12,

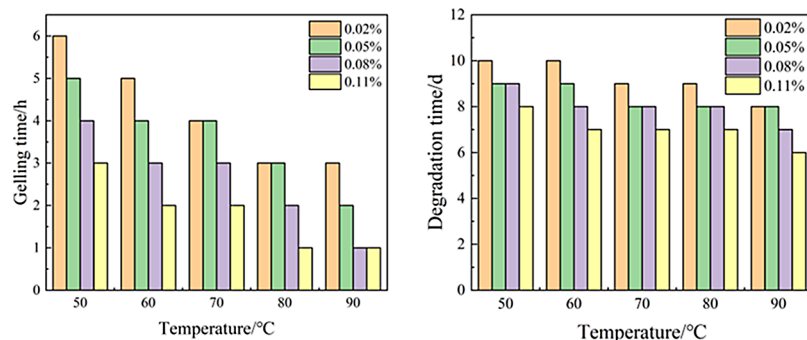


Figure 5. Influence of the Initiator Dosage on Hydrogel Properties.

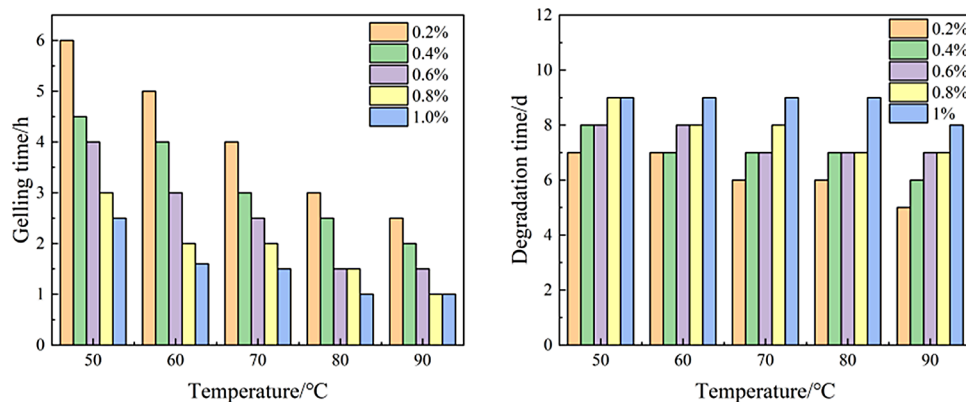


Figure 6. Effect of the dosage of cross-linking agent on the properties of the hydrogel.

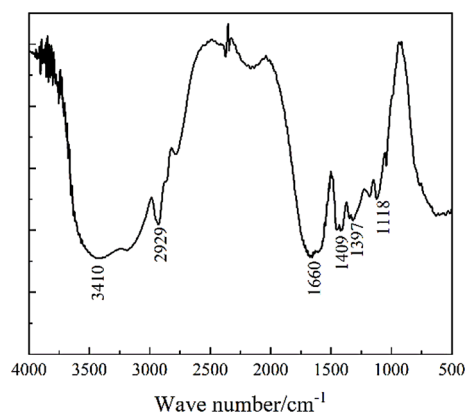


Figure 7. Infrared spectrum of hydrogels.

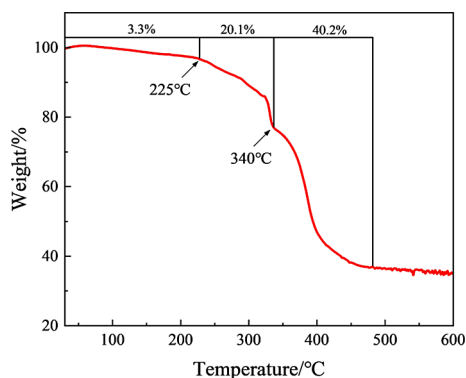


Figure 8. TGA analysis of the hydrogel temporary plugging agent.

Table 1. Effect of Temperature on Hydrogel Properties

temperature/ °C	gel strength									degraded viscosity/ mPa·s
	1d	2d	3d	4d	5d	6d	7d	8d	9d	
50	J	J	J	J	J	J	J	C	A	9.3
60	J	J	J	J	J	J	E	C	A	9.5
70	J	J	J	J	J	J	C	A	A	9.1
80	J	J	J	J	J	J	C	A	A	8.9
90	J	J	J	J	J	H	D	A	A	8.9

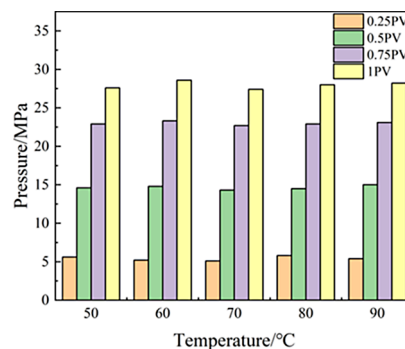


Figure 9. Pressure-bearing performance test of hydrogel under different injection volumes.

and 5.83, that of the proton connecting the ester group at 4.59, that of the proton connected to the nitrogen atom at 3.52, 3.30 and 4.50, and that of the proton on the benzene ring at 7.11. It can be seen from the spectrum that the synthesized cross-linking agent contains both carbon–carbon double bonds and ester groups, which conforms to the expected structure of the designed cross-linking agent.

Table 2. Experimental Results of Damage Performance of the Hydrogel Core

temperature/ °C	$K_1/(10^{-3}\mu\text{m}^2)$	$K_2/(10^{-3}\mu\text{m}^2)$	permeability recovery /%
50	1538.2	1502.7	97.69
60	1427.3	1393.2	97.61
70	1783.4	1718.9	96.38
80	1658.2	1602.7	96.65
90	1589.8	1526.3	96.01

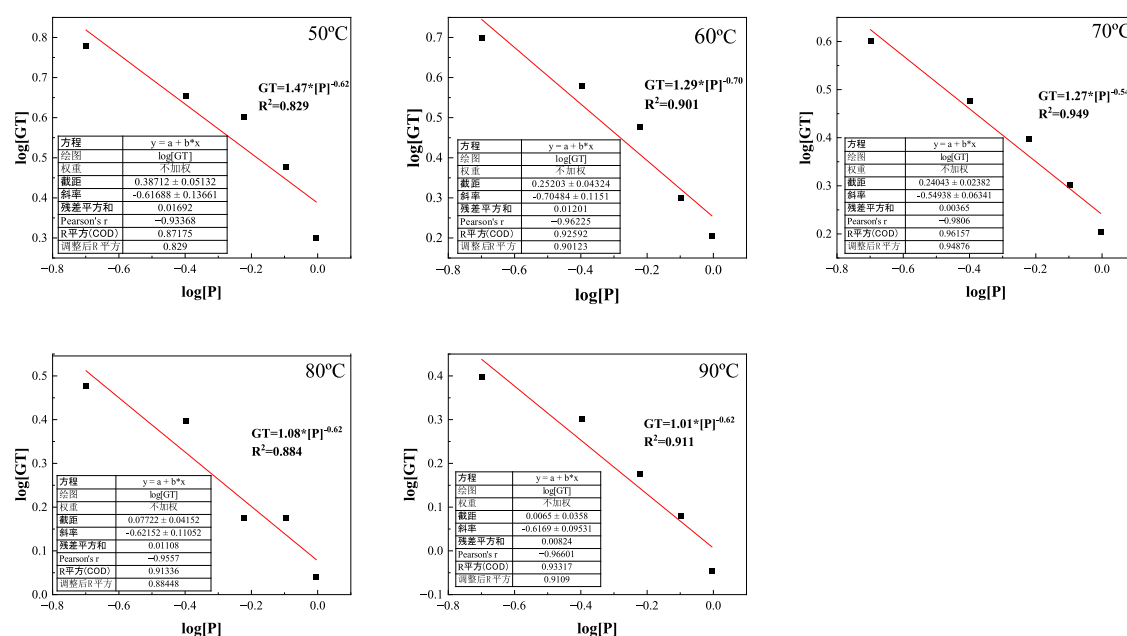
Table 3. Cross-Linking Agent Concentration-Gelation Time Relationship Table under Different Temperature Conditions

temperature/°C	cross-linker concentration/%				
	0.2%	0.4%	0.6%	0.8%	1.0%
50	6 h	4.5 h	4 h	3 h	2.5 h
60	5 h	3.8 h	3 h	2 h	1.6 h
70	4 h	3 h	2.5 h	2 h	1.5 h
80	3 h	2.5 h	1.5 h	1.5 h	1.1 h
90	2.5 h	2 h	1.5 h	1.2 h	0.9 h

3.1.3. Thermogravimetric Analysis. TGA of the cross-linking agent is shown in Figure 4, which indicates three stages in the decomposition of the cross-linking agent. The first stage is from room temperature to 210 °C, a process involving the loss of surface moisture and other volatile substances of the cross-linking agent, resulting in a weight reduction of 3%; the second stage, from 210 to 380 °C, is the main decomposition stage of the molecular chain of the cross-linking agent featuring the decomposition of the ester group of the molecular chain which leads to the breaking of the macromolecular chain and a weight reduction of 65%; the third stage, at above 380 °C, points to the final residue of part of the carbide and other ash contents. It can be concluded from the figure that the cross-linking agent shows good thermal stability under the condition of 210 °C and therefore boasts excellent thermal endurance.

3.2. Preparation of Hydrogels. 3.2.1. Initiator Dosage Optimization. At a temperature of 50–90 °C, a basic hydrogel formula of 10% monomer + 0.5% cross-linking agent + 0.5% reinforcing agent + initiator is adopted to examine the effect of the dosage of the initiator on the gelation performance and degradation performance of the hydrogel system. The experimental results in Figure 5 show that with the increase of the initiator dosage, the gelation time and degradation time of the hydrogel system are gradually shortened. At 90 °C, the increase of initiator dosage from 0.02 to 0.11% has resulted in the shortening of the gelation time from 3 to 1 h, and that of the degradation time from 8 to 6 days. This is because, with the increase of the initiator concentration, the concentration of free radicals in the hydrogel system increases, leading to a higher probability of free radical collision and a higher rate of polymerization. As a result, the gelation time becomes shorter and the polymerization rate too fast, leading to a lower polymerization degree of the system, lower hydrogel strength, and shorter degradation time. It can also be seen from the figure that the more the initiator dosage, the shorter the gelation time, and the higher the temperature, the faster the gelation time. This shows that controlled hydrogel gelation time and degradation time can be realized by controlling the dosage of cross-linking agent, so as to meet the needs of reservoirs with different temperatures. When the initiator dosage is higher than 0.08%, the initiator exerts a greater influence on the degradation performance of the hydrogel system; and the initiator dosage less than 0.05% leads to a too slow gelation time of the hydrogel system; therefore, the initiator dosage is set at 0.05%. At this time, the gelation time of gel is 2–5 h, and the degradation time is 8–10 days.

3.2.2. Cross-Linking Agent Dosage Optimization. At a temperature of 50–90 °C, a basic hydrogel formula of 10% monomer + 0.05% initiator + 0.5% reinforcing agent + cross-linking agent is adopted to examine the influence of the dosage of cross-linking agent on the gelation performance and degradation performance of the hydrogel system. As shown in Figure 6, the experimental results indicate an inverse relation

**Figure 10.** Curve fitting of cross-linking agent concentration and gelation time.

between the gelation time of the hydrogel system and the dosage of the cross-linking agent and a proportional relation between degradation time and the dosage of the cross-linking agent when the mass fraction of the monomer is 10% and that of the initiator is 0.05%. At 90 °C, the increase of the cross-linking agent dosage from 0.2 to 1% leads to a shortening of the gelation time of the hydrogel from 2.5 to 1 h and an extension of degradation time from 5 to 8 days. The reason for this phenomenon is that when the dosage of the cross-linking agent is low, the density of the system cross-linking agent is small, resulting in difficult cross-linking of the system. With the increase of the cross-linking agent dosage, the cross-linking of the system becomes easier, facilitating the formation of a good three-dimensional network cross-linking structure in the hydrogel system and thereby shortening the gelation time but prolonging the degradation time.³³ It can be seen from the figure that when the cross-linking agent dosage is 0.6%, the gelation time is moderate and has little effect on the degradation time; therefore, the initiator dosage is set at 0.6%.

3.3. Performance Evaluation of Hydrogels. **3.3.1. FT-IR Analysis.** The infrared spectrum of the hydrogel is shown in Figure 7, which indicates 3210 and 1660 cm^{-1} as the $-\text{NH}_2$ absorption peaks in the amide bond, the characteristic absorption peak of acrylamide; 2967 cm^{-1} as the stretching vibration peak of C–H in the double bond; 1409 cm^{-1} as the in-plane bending vibration peak of C–H in the double bond; and 1397 and 1118 cm^{-1} as the C–O stretching vibration absorption peaks in the ester group. The above analysis leads to the conclusion that the characteristic absorption peaks of amide groups and ester groups appear in the infrared image of the hydrogel, but without any sign of C=C absorption peaks. This indicates that the hydrogel has cross-linked by acrylamide and quaternary ammonium ester cross-linkers by breaking the C=C double bond.

3.3.2. TGA Analysis. The reservoir temperature of the hydrogel temporary plugging agent can not affect its molecular structure during plugging operation, so TGA is used to conduct thermal stability analysis on the temporary plugging agent, and the thermogravimetric analysis curve is shown in Figure 8. As can be seen from Figure 8, the thermal decomposition of the temporary plugging agent is mainly divided into three stages: the first stage is room temperature ~ 225 °C, which is mainly the volatilization process of the moisture on the surface of the temporary plugging agent, and the weight is reduced by 3.3%; the second stage is from 225 to 340 °C, which is mainly due to the decomposition of amide and ester bonds in the molecular structure of the temporary plugging agent, resulting in a decrease in mass and a weight reduction of 20.1%; the third stage is above 340 °C, which is mainly due to the decomposition of the main chain of the temporary plugging agent, resulting in a decrease in weight by 40.2%. From the thermogravimetric curve, it can be seen that the temporary plugging agent has good thermal stability and can meet the requirements of the vast majority of medium- and low-temperature reservoirs.

3.3.3. Evaluation of Temperature Resistance. The gel system prepared according to the optimal formula in the above study is placed in constant temperature water baths at 50, 60, 70, 80, and 90 °C, respectively, with the state of the gel observed at regular intervals to examine the thermal stability of the hydrogel system at a reaction temperature of 50–90 °C. The experimental results are shown in Table 1.

It can be seen from the table that the maximum strength of the hydrogel system can reach grade J at 50–90 °C, indicating high gel strength under different temperature conditions. The increase in temperature brings about a longer time required for the hydrogel system to reach grade A. This is mainly because as the temperature rises, the molecular thermal motion is intensified, resulting in higher collision probability between water molecules and the ester groups and amide groups in the hydrogel and consequently an accelerated hydrolysis rate of the ester groups and amide groups, with accordingly shorter degradation time. From the above results, it can be seen that the gelation time of the hydrogel system can be stabilized at 2–3 h at 50–90 °C, the strength can be maintained for 5–10 days upon completion of gelation, and the viscosity after complete degradation is lower than 10 mPa·s, indicating high thermal stability of the hydrogel system.

3.3.4. Plugging Performance Evaluation. The results of the plugging experiment of the hydrogel are shown in Figure 9, which indicates the gradually improving bearing performance of the hydrogel with the increase of injection volume from 0.25 to 1 PV, raising the bearing pressure from 5 to 28 MPa. When the injection volume of the hydrogel is less than 0.5 PV, the bearing pressure only reaches 15 MPa, but when the injection volume is 1 PV, the bearing pressure of the hydrogel exceeds 25 MPa, without exception, showing high pressure-bearing performance of the prepared hydrogel. It can also be seen from the figure that the breakthrough pressure of the hydrogel system is related to the injection volume but has nothing to do with the gelation temperature, showing that the hydrogel boasts high bearing performance which is not subject to temperature changes.

3.3.5. Core Damage Performance Test. In order to study the core damage performance of the hydrogel, fractured cores have been selected for displacement experiments under different temperature conditions. The experimental results are shown in Table 2 below, which indicates the permeability recovery values of hydrogels after self-degradation higher than 95% under different temperature conditions, with no exception. This is because the amide group and ester group in the hydrogel structure undergo hydrolysis under certain temperature conditions, leading to the complete degradation of the hydrogel into a low-viscosity liquid and showing that the hydrogel system can meet the different temperature requirements of oil reservoirs. According to the industry standard, a core damage rate of less than 5% is defined as having no impact on the reservoir, which also shows that the hydrogel system can, on the one hand, protect the reservoir well during actual operation and, on the other hand, reduce environmental pollution.

3.4. Study on Gelation Kinetics of the Hydrogel. Under the condition of 50–90 °C, the influence of the concentration of the cross-linking agent in the hydrogel system on gelation time has been investigated through a formula of 10% monomer dosage, 0.05% initiator dosage, and 0.5% reinforcing agent dosage with cross-linking agent concentration, respectively, at 0.2, 0.4, 0.6, 0.8, and 1.0%. The experimental data are shown in Table 3, and the fitting curve is shown in Figure 10. It can be seen from Table 3 that when the cross-linking agent concentration is 0.2% \sim 1%, the gelation time of the hydrogel system shortens with the increase of the cross-linking agent concentration. This is because, with the increase of the mass fraction of the cross-linking agent, the number of groups that can undergo cross-linking reactions also

risers, resulting in higher speed of the cross-linking reaction and shorter gelation time of the gel system. It can be seen from Figure 10 that under the condition of 50–90 °C, there are

$$50\text{ }^{\circ}\text{C}: \text{GT} = 1.47 \times [\text{P}]^{-0.62}, \quad R^2 = 0.829$$

$$60\text{ }^{\circ}\text{C}: \text{GT} = 1.29 \times [\text{P}]^{-0.70}, \quad R^2 = 0.901$$

$$70\text{ }^{\circ}\text{C}: \text{GT} = 1.27 \times [\text{P}]^{-0.54}, \quad R^2 = 0.949$$

$$80\text{ }^{\circ}\text{C}: \text{GT} = 1.08 \times [\text{P}]^{-0.62}, \quad R^2 = 0.884$$

$$90\text{ }^{\circ}\text{C}: \text{GT} = 1.01 \times [\text{P}]^{-0.67}, \quad R^2 = 0.911$$

Among them, GT refers to the gelation time of the gel system, recorded by the hour, and P refers to the mass concentration of the cross-linking agent, recorded by percentage (%). It can be seen that under the condition of 50–90 °C, the order of reaction between the concentration of the cross-linking agent and the gelation time is about 0.6.

4. CONCLUSIONS

In this work, a quaternary ammonium ester cross-linker was synthesized from dimethylamino ethyl acrylate and dibromo-p-xylene and analyzed by FT-IR, ¹H NMR, and TGA. Based on the synthesized quaternary ammonium ester cross-linking agent, the temporary plugging agent formulations under different temperature conditions were obtained through the optimization of initiator and cross-linking agent additions. The performance evaluation of the temporary plugging agent was carried out, and the experimental results showed that its adhesive strength could be maintained at 50–90 °C for 5–10 days, and the viscosity was lower than 10 mPa·s after complete degradation. The hydrogel temporary plugging agent has good pressure bearing performance and reservoir protection performance, and the damage rate to the core is below 5%, which can be applied to medium- and low-temperature well-killing operations. Finally, the gelation kinetics of the hydrogel plugging agent system was studied, and the kinetic equation between the concentration of the cross-linking agent and the gelation time was obtained at 50–90 °C. The reaction order between the concentration of the cross-linking agent and the gelation time was about 0.6.

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Notes

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REFERENCES

- (1) Hao, T. C.; Zhong, L. G.; Liu, J. B.; et al. Design method and application of accurate adjustment scheme for water injection wells around adjustment wells. *J. Pet. Explor. Prod. Technol.* **2022**, *12* (3), 743–752.
- (2) Ma, X.; Li, H. T.; Luo, H. W.; et al. Research on well selection method for high-pressure water injection in fractured-vuggy carbonate reservoirs in Tahe oilfield. *J. Pet. Sci. Eng.* **2022**, *214*, No. 110477.
- (3) Gong, N.; Jia, L. X.; Li, J.; et al. Causes and Countermeasures of Annular Pressure in Water Injection Wells under Injection Conditions. *China Pet. Mach.* **2018**, *46* (11), 91–96.
- (4) Ji, R.; Yu, X.; Yang, H.; et al. Preparation and degradable mechanism of self-breaking gel valve for underbalanced drilling. *Geoenergy Science and Engineering* **2024**, *235*, No. 212705.
- (5) Huang, Z.; Yang, H.; Ye, Z.; et al. Preparation and enhanced oil recovery study of amphiphilic Janus nanosheets. *J. Mol. Liq.* **2024**, *400*, No. 124524.
- (6) Li, D.; Li, F.; Liu, J.; et al. Synthesis and properties of PAM/PLA composite degradable particle temporary plugging agent. *J. Appl. Polym. Sci.* **2022**, *139* (48), No. e53216.
- (7) Liu, C.; Zou, H.; Wang, Y.; et al. Degradation behavior and mechanism of P (AM/AA/AMPS)@PLA core-shell self-degrading temporary plugging agent. *J. Mol. Liq.* **2024**, *393*, No. 123656.
- (8) Zhu, D.; Gong, Y.; Wang, J.; et al. Effect of Crosslinker Types on Temporary Plugging Performance of Degradable Preformed Particle Gels for Unconventional Petroleum Reservoir Development. *Energy Fuels* **2023**, *37* (1), 373–384.
- (9) Wang, K.; Liu, G.; Guo, Y.; et al. Preparation and properties of degradable hydrogels as a temporary plugging agent used for acidizing treatments to enhance oil recovery. *Colloids Surf, A* **2022**, *637*, No. 128218.
- (10) Pan, Y.; Cui, X.; Wang, H.; et al. Research Progress of Intelligent Polymer Plugging Materials. *Molecules* **2023**, *28* (7), 2975.
- (11) Lashari, Z. A.; Yang, H.; Zhu, Z.; et al. Experimental research of high strength thermally stable organic composite polymer gel. *J. Mol. Liq.* **2018**, *263*, 118–124.

- (12) Yang, S.; Liu, Z.; Pan, Y.; et al. A Review of Research Progress on the Performance of Intelligent Polymer Gel. *Molecules* **2023**, *28* (10), 4246.
- (13) Lashari, Z. A.; Yang, H. B.; Zhu, Z.; et al. Experimental research of high strength thermally stable organic composite polymer gel. *J. Mol. Liq.* **2018**, *263*, 118–124.
- (14) Huang, Z.; Yang, H.; Zheng, L.; et al. Preparation of amphiphilic Janus nanosheets based on thermally expandable microspheres and evaluation of their physical and chemical properties. *Fuel* **2024**, *358*, No. 130253.
- (15) Zhao, S.; Zhu, D.; Bai, B. Experimental study of degradable preformed particle gel (DPPG) as temporary plugging agent for carbonate reservoir matrix acidizing to improve oil recovery. *J. Pet. Sci. Eng.* **2021**, *205*, No. 108760.
- (16) Mao, Y.; Anand, L. A theory for fracture of polymeric gels. *Journal of the Mechanics and Physics of Solids* **2018**, *115*, 30–53.
- (17) Zhang, S.; Wei, F.; Liu, P.; et al. Plugging mechanisms of polymer gel used for hydraulic fracture water shutoff. *e-Polym.* **2020**, *20* (1), 411–422.
- (18) Bai, Y.; Shang, X.; Wang, Z.; et al. Experimental study of low molecular weight polymer/nanoparticle dispersed gel for water plugging in fractures. *Colloids Surf., A* **2018**, *551*, 95–107.
- (19) Zhang, D.; Wei, J.; Fang, X. Study on the variation of rock pore structure after polymer gel flooding. *e-Polym.* **2020**, *20* (1), 32–38.
- (20) Wu, W. P.; Hou, J. R.; Qu, M.; et al. A novel polymer gel with high-temperature and high-salinity resistance for conformance control in carbonate reservoirs. *Petroleum Science* **2022**, *19* (6), 3159–3170.
- (21) Lu, S.; Bo, Q.; Zhao, G.; et al. Recent advances in enhanced polymer gels for profile control and water shutoff: A review. *Front. Chem.* **2023**, *11*, No. 1067094.
- (22) Freedman, B. R.; Uzun, O.; Luna, N. M. M.; et al. Degradable and Removable Tough Adhesive Hydrogels. *Adv. Mater.* **2021**, *33* (17), No. 2008553.
- (23) Jia, H.; Yang, X. Y.; Zhao, J. Z. Development of a Novel In-Situ-Generated Foamed Gel as Temporary Plugging Agent Used for Well Workover: Affecting Factors and Working Performance. *SPE Journal* **2019**, *24*, 1757–1776.
- (24) Wu, H.; Ge, J.; Yang, L.; et al. Developments of polymer gel plug for temporary blocking in SAGD wells. *J. Pet. Sci. Eng.* **2022**, *208*, No. 109650.
- (25) Amir, Z.; Said, I. M.; Jan, B. M. In situ organically cross-linked polymer gel for high-temperature reservoir conformance control: A review. *Polym. Adv. Technol.* **2019**, *30*, 13–39.
- (26) El-Karsani, K. S.; Al-Muntasheri, G. A.; Hussein, I. A. Polymer systems for water shutoff and profile modification: a review over the last decade. *SPE Journal* **2014**, *19* (01), 135–149.
- (27) Zhang, B. B.; Yang, H.; Chen, P.; et al. Quaternary-ammonium-based supramolecular gel for temporary plugging diversion fracturing. *Colloids Surf., A* **2023**, *665*, No. 131174.
- (28) Sydansk, R. D.; Smith, T. B. Field Testing of a New Conformance-Improvement-Treatment Chromium (III). *Gel Technol.* **1988**, 699–707.
- (29) Nutan, B.; Chandel, A. K. S.; Bhalani, D. V.; et al. Synthesis and tailoring the degradation of multi-responsive amphiphilic conetwork gels and hydrogels of poly(β -amino ester) and poly(amido amine). *Polymer* **2017**, *111*, 265–274.
- (30) Wei, W.; Wu, M.; Shang, N.; et al. Low temperature preparation of high-performance citric acid crosslinked starch gels with adjustable properties based on cationic esterification synergistic crosslinking. *Food Hydrocolloids* **2023**, *145*, No. 109098.
- (31) Chen, J.; Ao, Y.; Lin, T.; et al. High-toughness polyacrylamide gel containing hydrophobic crosslinking and its double network gel. *Polymer* **2016**, *87*, 73–80.
- (32) Zou, C.; Dai, C.; Liu, Y.; et al. A novel self-degradable gel (SDG) as liquid temporary plugging agent for high-temperature reservoirs. *J. Mol. Liq.* **2023**, *386*, No. 122463.
- (33) Wang, Q.; Cai, J.; Wang, J.; et al. Development and Application of the Anti-High-Temperature Delayed Crosslinking Polymer as a Gel Plugging Additive for Drilling Fluid. *Gels* **2024**, *10* (1), 73.